Paper Technology/Reduced Sidestream Plan

February 15, 1990

I. Introduction

The paper technology program has as its overall objective the development of proprietary cigarette papers for new products. The specific applications at this time are: 1) products with reduced sidestream visibility; 2) products for aroma modification of sidestream; 3) papers which will allow control of burn rate for Project Tomorrow; 4) development of filter materials which can be used to make filters with surface areas equivalent to paper filters, but with surface adsorption characteristics similar to cellulose acetate At this time the first goal, cigarettes with reduced sidestream visibility, is by far the highest priority. Consequently the majority of this plan will be devoted to that topic. Plans regarding the remaining three topics are restricted to the specific areas involving the development of new papers.

II. Products with Reduced Sidestream Visibility

A. Objectives

1. To develop a proprietary cigarette wrapper which will reduce visible sidestream smoke by at least 70% in a full circumference cigarette, as compared to an appropriate control, with acceptable subjectives by 1990.

2. To develop proprietary cigarette wrappers which will in addition to reducing sidestream visibility will reduce sidestream odor and irritation.

The second objective has been added in 1990. Little work is planned to take place addressing this objective in 1990. It is anticipated, however, that by the end of 1990 several satisfactory prototypes with reduced visibility will have been completed. Resources will then be phased into development of products with reduced odor and irritation. A brief outline of the plans for this phase of the project for 1991 and following years is given in Appendix A.

B. Introduction and Status

Philip Morris has been working on cigarettes with reduced sidestream visibility for about eight years. Work was initiated with the introduction of a commercial reduced sidestream brand, Passport, in Canada, and has grown in importance during the intervening years as a consequence of the public's growing, although misplaced, concern over passive smoke. Passport utilized a paper manufactured by Ecusta containing 12% magnesium hydroxide. The product had serious subjective problems and was not a commercial success. During the first five years that R&D has been involved in a reduced sidestream program we depended on our two suppliers, Ecusta and Kimberly-Clark, to provide us with low sidestream papers. Three years ago, however, a decision

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was made to attempt to develop our own low sidestream paper. This was done first of all because our suppliers have not been strikingly successful in providing us with a paper which will achieve our objectives. More importantly, however, is that it is essential that we develop our own proprietary paper to obtain a clear competitive advantage. In 1989 we developed a slim cigarette with sidestream reduction which met our target and acceptable subjectives. This product utilizes a double wrap system. The outer wrap was developed jointly by PM and Kimberly-Clark. It has a 45 g/m^2 basis weight, contains 35% calcium carbonate with a surface area of 20 m^2/g, and contains potassium succinate, monoammonium phosphate (MAP) and sodium carboxymethyl cellulose (CMC) as additives. The inner wrap is a thin (18 g/m^2) paper with 3% low surface area calcium carbonate and 2% potassium citrate. This product was introduced nationally in September, 1989, and appears to be doing reasonably well. Neither the system used on the slim cigarette nor the Ecusta magnesium hydroxide paper, however, has proved to be satisfactory for a full circumference cigarette. The best sidestream visibility reduction which has been achieved for a full circumference cigarette using the double wrap system is about 65%, below our target of 70%. In addition, there are clear taste problems. The magnesium hydroxide wrapper will give greater than 70% sidestream visibility reduction, but with severe subjective problems. Not only are there definite taste problems, but ash flaking problems as well. Despite the drawbacks of the magnesium hydroxide wrapper, RJR recently test marketed a low sidestream product, Vantage Excel. We regard this product to be unacceptable, and the product was withdrawn from test market in late 1989.

It can be concluded from the above discussion that the only way in which PM can successfully reach the goal of an acceptable full circumference product with greater than 70% sidestream visibility reduction is to design our own paper. In order to accomplish this goal we needed to develop certain resources to allow us to carry out research and development in the area of paper technology. In the past year we have built and equipped an in-house facility to fabricate hand sheets using flax fibers; we have negotiated a contract with the University of Maine to make pilot quantities of papers; we have developed an in-house inorganic chemistry group to investigate the chemistry of paper fillers; we have initiated work in the area of sol-gel chemistry to develop inorganic fillers with novel morphologies and surface charge, and have obtained consultants to assist us with this work; we have installed a sidestream chamber, similar to the facility at Neuchatel, to be able to carry out studies on sidestream smoke; we have designed and built an eight-port smoking apparatus to rapidly measure sidestream visibility; and we have put our two major paper suppliers on notice that we plan to conduct programs with them in a collaborative manner, so that we receive exclusivity on any papers which may result from such programs. In order to achieve the objective of developing a proprietary paper which will reduce sidestream visibility in a full circumference cigarette, we have delineated seven major strategies. These strategies are:

1. Develop "high basis weight" papers as low sidestream wrappers for full circumference cigarettes.

2. Investigate and develop alternate inorganic fillers.

3. Investigate and develop alternate fluxing agents.

4. Carry out fundamental studies to determine the mechanism by which low sidestream papers reduce sidestream visibility.

5. Develop and optimize products using experimental papers.

6. Define the subjective and analytical characteristics of mainstream smoke from a calcium carbonate, dual wrap low sidestream prototype compared to an appropriate control.

7. Characterize the chemistry of sidestream smoke from existing brands, new products and prototypes using the new sidestream chamber.

An eighth strategy discussed in last year's plan - develop techniques for measuring visible sidestream smoke and sidestream particulates - is no longer included, since we have completed our work on this strategy.

Each of these strategies will be discussed below. A brief discussion of current status will be given followed by the specific tactics, along with target dates, which will be used to realize each strategy.

C. Strategies and Tactics

1. Develop "high basis weight" papers as low sidestream wrappers for full circumference cigarettes

a. Status

Development of a paper to yield a 65-70% reduction in sidestream visibility for a 24.8 mm circumference 100 mm cigarette has been the primary objective for this strategy during the past quarter. As was mentioned in the June, 1989, plan the original objective of this strategy was to determine if a dual wrap system could be replaced with a single wrap. Two types of wraps were investigated. One was a "bilayer" sheet made with a dual headbox system in such a way so that there was a difference in calcium carbonate levels between the inner and outer portions of the sheet. The second was a paper made to the same basis weight (63 g/m^2) as the bilayer sheet, but with a uniform distribution of the calcium carbonate. This latter sheet is called a "high basis weight" paper. The basis weight of 63 g/m^2 was chosen since it was the sum of the two wraps used for Trim V. Of the two types of paper, the high basis weight paper has given the more promising results. Considerable work with this paper has shown that to achieve significant sidestream reduction it is necessary to have a low porosity sheet (3-5 Coresta), a high concentration of potassium must be used, and a sufficient

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level of an appropriately chosen inorganic salt must be added to function as a burn retardant. The best results have been obtained by coating the paper with between 10 and 12% mono potassium phosphate. The potassium phosphate acts both as a source of potassium ion to provide good sidestream reduction and as a burn retardant. Although other potassium or sodium salts will give similar sidestream reductions, mono potassium phosphate has provided cigarettes with the best subjectives to date. A number of different models have been made, and sidestream reductions range from 65-68%.

An agreement has been signed by Kimberly-Clark giving PM exclusive use of this paper for a two year period. A patent covering this paper has also been filed. Kimberly-Clark has supplied us with 500 pounds of four papers with the following specifications: basis weight, 63 g/m^2; porosity, 2.9 and 4.2 Coresta; inorganic filler, Multifex MM calcium carbonate; level of inorganic filler, 26 and 36%. Cigarettes were made from these four papers using an amount of mono potassium phosphate calculated to give equal sidestream reduction. Based on subjective evaluation of these models, paper E2560 (4.2 Coresta, 36% calcium carbonate) has been selected for further work. Ongoing studies designed to optimize the subjective response of cigarettes made with this paper include screening of new blends, development of new aftercut flavors and casings, investigation of other additives on the wrappers to reduce sidestream irritability, optimization of packing density, and studies on the correlation of filler OV with subjective response.

New blend formulations have been developed by the Leaf Department in an effort to improve the tobacco character of the cigarette. Blend 218 gave improvements in subjective performance, but fell short of the sidestream reduction target. Blend 231 was formulated based on the 218 blend using more recon to reduce visible sidestream smoke. Testing of the 218 blend is in progress. An aftercut formulation containing methyl jasmonate was recommended by Flavor Development and is being tested on Marlboro blend, our standard reference blend. Initial sidestream panel testing indicates a significant difference in ratings for the methyl jasmonate aftercut. Further testing will tell whether the difference is in the direction of more tobacco character. Several materials have been added to the paper in order to reduce both sidestream irritability and mainstream "paper taste." These materials include sugars, MAP, MAP plus fructose, amino acids and lactic acid. Most promising have been the lactic acid samples. Further work is planned in this area.

One frequent response to cigarettes made with the high basis weight paper is 'dry taste.' To determine if the heavily sized paper extracts water from the tobacco, filler OV's were measured on packaged cigarettes with both

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conventional and 65 g/m^2 wrappers after 6 and 12 weeks of storage at laboratory conditions. No difference in filler OV was found between the two wrappers. Conventional and 65 g/m^2 papers were equilibrated at 60% relative humidity and tested for moisture content; both contained 6% OV. Lastly, cigarettes stored under two different types of conditions which differed by at least one OV unit were smoked subjectively. No major difference could be perceived between the two models. Therefore, the dry taste does not appear to be caused by an altered distribution of moisture in the cigarette. No further work will be done in this area except to determine an optimum OV level once a satisfactory model has been developed.

b. **Tactics and timetable**

(1) Complete investigation of different blends including Blend 231, Blend 213, and the L&M blend - first quarter, 1990.

(2) Continue to develop and evaluate new aftercut flavors based on methyl jasmonate - second quarter, 1989.

(3) Optimize the level of lactic acid on the wrapper, and investigate the use of other organic acids including levulinic acid, malic acid, malonic acid, and tartaric acid - fourth quarter, 1989.

(4) Investigate the use of additives on the wrapper which will "chemically scrub" aldehydes, such as a cooked flavor type system and a β-amino alcohol - second quarter, 1990.

(5) Develop potential casings containing lactic acid and other organic acids - second quarter, 1990.

(6) Conduct study to determine optimum filler packing density - second quarter, 1990.

(7) POL test most promising model - second quarter, 1990.

(8) Develop high basis weight papers for use on Japanese products - second quarter, 1990.

(9) Investigate the effect of Ambrosia additives on cigarettes made with high basis weight papers - second quarter, 1990.

(10) Evaluate promising sizing agents on calcium carbonate papers for analytical smoking and subjective performance - continuing.

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2. **Investigate and develop alternate inorganic fillers**

a. **Status**

Research into development of alternate inorganic fillers for sidestream reduction can be divided into four general areas. The first is the synthesis of inorganic oxides/ carbonates through the sol-gel process. This method was selected for investigation since it can be controlled so that very small, high surface area particles with potentially novel morphologies are produced. Initial results obtained during the latter part of the fourth quarter, 1989, indicated that a novel composition of matter, comprised of hydromagnesite [$Mg_5(CO_3)_4(OH)_2$ 4-5H_2O] and magnesium hydroxide in an intimate mixture, led to excellent sidestream reduction in a cigarette which had acceptable subjective properties and excellent ash formation. A number of sol-gel routes have subsequently been employed to prepare compositions having hydromagnesite and/or magnesium hydroxide with a goal of developing a proprietary inorganic filler having the properties described above. It is important to note that there are no reports in the literature regarding gels from magnesium carbonates. Hence, patent protection should be available not only for processes, but for compositions of matter.

We are currently pursuing our immediate objective; namely, to reproduce the initial studies. We are also examining all possible sol-gel routes to materials having these magnesium carbonate/magnesium hydroxide compositions with a goal of developing a procedure which can be performed on a commercial scale. By careful examination of the phase diagrams involved and evaluating the role of kinetic control vs. thermodynamic control, we plan to achieve these objectives.

The sol-gel approach is now only one of a number of approaches to the development of new inorganic fillers for sidestream reduction. We are taking the best leads from our sol-gel research and attempting to prepare identical and/or related compositions using other procedures. Thus, the second approach is the synthesis and evaluation of inorganic compounds with chemical properties significantly different from calcium carbonate or brucite (magnesium hydroxide). Promising results have been obtained for hydromagnesite and magnesite. Most of the effort during the first quarter will be placed on various phases of magnesium carbonate. We will be investigating different routes for the synthesis of hydromagnesite/magnesium hydroxide/magnesite compositions. If requested , we will prepare additional quantities of magnesite by hydrothermal methods (see below) for larger-scale testing.

The third approach is the use of alternate techniques for the synthesis of inorganic materials in order to determine how the method of synthesis alters chemical composition and physical properties. Techniques which will be used are hydrothermal synthesis and spray/flow pyrolysis. Hydrothermal techniques have been used to prepare magnesite, a pure magnesium carbonate which has been shown to be a fine sidestream reductant. Another technique which is being used, although not truly a technique for synthesis, is sonication. Sonication can break up agglomerates of solids, initiate nucleation, and/or reduce particle size. Consequently, certain materials may function more effectively to reduce sidestream. Freeze drying has now been found to effectively produce materials which lead to more porous paper.

The fourth approach is the direct modification of paper or of substances, e.g., flax, which are used to make paper. For example, one of the important leads from our sol-gel studies is that compositions of magnesium hydroxide and hydromagnesite significantly reduce sidestream visibility. Since we have been able to convert magnesium hydroxide to hydromagnesite in the presence of carbon dioxide, we anticipate that we could form intimate mixtures of these two substances by treating paper containing magnesium hydroxide with carbon dioxide.

Studies have been designed to determine why certain inorganic fillers are effective while others are not. Previous hypotheses which have addressed this question, namely, the role of filler surface area and the requirement that the filler undergo some type of reaction or phase change, have not proven out. Recently, the hypothesis that there is an interaction between the inorganic filler and the fluxing agent to form a ceramic has been advanced. Although our original thought was that this interaction may have involved sintering, further investigations indicate that the key step may be liquifaction of the fluxing agent. This hypothesis will be investigated further with the ultimate goal of developing a rapid screening method for the identification of promising new inorganic fillers or fluxing agents.

b. Tactics and Timetable

(1) Sol-Gels

(a) Carry out lab scale-up of the most promising sol-gel derived mag carbonate particles to allow larger scale evaluations in reduced sidestream papers - first quarter, 1990.

(b) Determine the detailed chemical and physical structure of the material obtained in part (a) including particle morphology, particle size,

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surface charge, and crystallographic information - second quarter, 1990.

(c) Complete synthesis and evaluation of sol-gels involving magnesium hydroxide/magnesium oxide/ hydromagnesite in both water and alcohol;-determine optimum conditions for preparation of solids from at least two procedures - second quarter, 1990.

(d) Evaluate papers made using these particles - third quarter, 1990.

(e) Fully characterize chemical/physical structures of sol-gels already obtained including X-ray diffraction, Raman spectroscopy, infrared spectroscopy and TGA - continuing.

(f) Develop analytical techniques, such as small angle scattering and light scattering, to determine the size and shape of the developing polymer during the sol to gel transition - continuing.

(2) Other inorganic fillers

(a) Fully evaluate hydrothermal synthesis to obtain novel inorganic filler compositions starting with combinations of hydromagnesite, magnesium oxide, magnesium hydroxide, and/or magnesite in the presence of water and carbon dioxide - first quarter, 1990.

(b) Treat paper, flax, and other paper precursors, which have been previously treated with magnesium hydroxide, with carbon dioxide to partially react the magnesium hydroxide - second quarter, 1990.

(c) Continue joint development program with Ecusta on hydromagnesite/magnesite papers - continuing.

(d) Locate a commercial source for coprecipitated magnesium hydroxide/calcium carbonate or calcium carbonate precipitated on fine magnesium hydroxide particles - second quarter, 1990.

(e) Synthesize, characterize, and evaluate compounds selected - continuing.

(f) Investigate catalytic systems - continuing.

(3) Alternate methods of synthesis

(a) Investigate the interaction of the fluxing agent with the inorganic filler in order to develop

a rapid screening system for new fillers or fluxing agents - second quarter, 1990.

(b) Investigate the feasibility of spray pyrolysis or flow pyrolysis as a technique for the preparation of inorganic fillers for low sidestream papers, with an emphasis on magnesium compounds - second quarter, 1990.

(c) Investigate the effect of sonication and freeze drying on performance of a number of inorganic fillers with respect to sidestream reduction - continuing.

3. **Investigate and develop alternate fluxing agents**

a. **Status**

The November, 1989, plan discussed the role of the fluxing agent for calcium carbonate papers. To summarize: 1) a calcium carbonate low sidestream paper requires the presence of an alkali metal salt to achieve significant sidestream reduction; 2) the role of the fluxing agent is most likely to form a "ceramic sheath" by first melting and then solidifying; 3) as long as the fluxing agent is a low-melting solid, the sidestream reduction obtained will be solely a function of the potassium level - the nature of the anion plays no role. As a consequence of the latter fact, there was little likelihood of improving on mono potassium phosphate as a fluxing agent with respect to sidestream reduction. The situation with magnesium carbonate papers, however, is quite different.

Extremely interesting results have been obtained with magnesium carbonate papers using potassium citrate and potassium succinate as fluxing agents. Magnesite papers give improved sidestream reduction with potassium citrate as opposed to potassium succinate at basis weights over 45 g/m^2. The situation is reversed for hydromagnesite, where potassium citrate is virtually ineffective, but potassium succinate works quite well. Sodium salts appear to be fore effective than potassium salts at equal molar levels for hydromagnesite papers. Sodium fumarate appears to be particularly interesting. At this time we have no explanation for these findings; however, these results clearly point out the importance of evaluating a given phase of magnesium carbonate with a series of fluxing agents. Studies are in progress to examine both magnesite and hydromagnesite papers with a series of fluxing agents at a range of levels. In addition, certain of these papers will be analyzed by electron microscopy both before and after burning. Plans for further work in this area cannot be formulated until the results from the studies proposed above have been obtained.

b. **Tactics and Timetable**

(1) Evaluate sidestream reduction with a variety of magnesium carbonate phases at a range of levels of the following alkali metal salts: potassium succinate, potassium citrate, sodium fumarate and other sodium salts, and potassium and sodium pyrophosphates - second quarter, 1990.

(2) Investigate the use of various sugars which are either already acidic or potentially could generate acidic products during combustion - second quarter, 1990.

(3) Complete screen of soluble iron compounds as potential fluxing agents - first quarter, 1990.

(4) Investigate the use of soluble calcium and magnesium compounds, particularly magnesium polyphosphates and soluble $Mg(H_2PO_4)_2$, as potential fluxing agents - second quarter, 1990.

4. **Carry out fundamental studies to determine the mechanism by which low sidestream papers reduce sidestream visibility**

a. **Status**

At this time only three types of mechanisms can be proposed to account for the reduction in visible sidestream smoke through the use of low sidestream cigarette papers. The first is that the particle size of the smoke is decreased so that light scattering properties change. If this were to occur, then the visibility would appear to decrease even though there may be little or no change in actual particulate matter. We have sufficient evidence at this time to indicate that this mechanism is not operative for the systems examined to date (calcium carbonate and magnesium hydroxide wrappers). First of all light scattering data has shown that there is no difference in the mean particle size or standard deviation for sidestream smoke from models made with either calcium carbonate or magnesium hydroxide compared to a normal cigarette. This finding will be independently confirmed using the sidestream chamber (see below). Secondly, in every case checked there is an excellent correlation between weight of sidestream particulate matter and visibility measurements.

The second mechanism postulates that the low sidestream wrapper forms a "ceramic sheath" (see above) around the coal which either forces the sidestream smoke down the rod, leading to increased mainstream TPM, or forces the smoke through the coal, resulting in increased sidestream gas phase. A study was carried out in 1989 wherein a mixture of ^{14}C-glucose and fructose was added to a full circumference calcium carbonate dual wrap cigarette and a single wrap

magnesium hydroxide cigarette. The results indicated that the mechanism of sidestream reduction for the calcium carbonate model was quite consistent with the "ceramic sheath" hypothesis. However, the mechanism for the magnesium hydroxide model was different. It is likely that the mechanism for magnesium carbonate wrappers is similar to that for magnesium hydroxide.

The last mechanism suggests that the combination of inorganic filler and "fluxing agent" is converting sidestream smoke at the char line to volatile components. This conversion could either be oxidative in nature (combustion to carbon dioxide and carbon monoxide) or pyrolytic (cracking of high molecular weight compounds to low molecular weight compounds). Since magnesium carbonate filled paper does not seem to be operating via a "ceramic sheath" type mechanism, it is likely that this mechanism is extremely important for magnesium carbonate papers. Therefore, it is in this area that most of the effort on elucidating mechanisms of sidestream reduction must be placed in the short term.

Longer term mechanistic work will examine in more detail the physical differences in the static burning of low sidestream models as compared to normal models. Specific areas include studies of thermal properties of the coal using both the IR camera and Schlieren photography, and neutron radiographic studies.

Work is continuing to determine if the previously observed increase in the surface area of paper chars is related to sidestream smoke reduction. Examinations are focusing on the effect of heat on the individual surface areas of the calcium carbonate and flax portions of cigarette paper, as well as the effect of selected sizing agents on the paper components. Preliminary work has involved the development of improved methods for heating samples and conducting the analyses. Results to date suggest that the interaction of the sizing agent with calcium carbonate upon heating is probably not the source of the increase in surface area. Investigation of cellulose/flax samples is currently in progress.

A study is in progress in collaboration with the University of Virginia Nuclear Engineering Department using neutron activation to examine the SS/MS smoke distribution of phosphorus from a low sidestream model cigarette made utilizing a high basis weight calcium carbonate paper sized with 11-12% mono potassium phosphate. The sidestream smoke from this cigarette model is somewhat irritating, and the cause may be due to phosphorus-containing compounds derived from the phosphate additive on the paper. The study involves neutron activation of empty cigarette paper tubes (and filters), insertion of a preformed roll of tobacco, followed by smoking and analysis of ^{32}P on sidestream and mainstream

TPM pads. Preliminary work has shown that the technique has the sensitivity needed for the model of interest. Knowing the transfer rate of phosphorus to the smoke streams may help us understand the source of the irritancy of the sidestream smoke.

Research studies will be initiated at the Solar Energy Research Institute (SERI) on the pyrolysis products of cigarette paper, in collaboration with Dr. Helena Chum. In particular a Box-Behnken design will be conducted to evaluate the effects of pH, temperature, and additive concentration on the pyrolysis products of the paper. Multivariate analysis will be used for data reduction of the mass-spectral patterns obtained from the triple quadrupole mass spectrometer at SERI. These statistical techniques are well-suited for evaluating complex systems in which many variables are exerting an effect simultaneously. They are also ideally suited for evaluating complex product distributions from biomaterials such as cellulose or tobacco. Additionally, definitive mechanistic studies will be conducted using <u>Acetobacter xylinum</u> from ^{13}C-labelled glucose substrates. These studies will provide unambiguous information regarding the effect of acids and bases on pyrolysis mechanisms and products.

b. Tactics and timetable

(1) Carry out neutron radiography studies to examine the SS/MS smoke distribution of phosphorus from a low sidestream model cigarette utilizing a high basis weight paper sized with mono potassium phosphate - first quarter, 1990.

(2) Examine the effects of different flax/cellulose refining conditions on the surface area of paper chars - second quarter, 1990.

(3) Initiate research at SERI on the pyrolysis products of cigarette paper as a function of pH, temperature, and additive concentration - first quarter, 1990.

(4) Investigate the possible correlation of the pH of mainstream smoke with the subjective characteristics of low sidestream cigarettes - second quarter, 1990.

(5) Choose three or four "marker compounds" in sidestream TPM, obtain compounds labelled with ^{14}C, add to tobacco, make cigarettes, and determine fate of label in low sidestream and standard models - long term study (one to three years).

(6) Carry out neutron radiography studies of both low sidestream and normal models in order to generate

tomographic reconstruction of the coal - fourth quarter, 1990.

5. **Develop and optimize products using experimental papers**

a. **Status**

When cigarettes made with an experimental paper show product potential in terms of sidestream reduction and analytical smoking results, and these results have been demonstrated on machine-made cigarettes, the cigarettes are evaluated subjectively to further assess product potential. Typically, the cigarettes are found lacking in one or more subjective attribute, and work is undertaken to improve subjective performance while maintaining the sidestream reduction. Through the combined efforts of Cigarette Technology, Cigarette Development, Flavor Development, and the Leaf Department, models with modified papers, blends, flavors, and constructions are fabricated and evaluated. Attention is also given to developing a commercial source of the paper so that a market introduction could be implemented rapidly if warranted.

Currently all of the effort directed toward this strategy involves the optimization of high basis weight calcium carbonate papers. Most of the tactics have already been covered under strategy number 1. There are three specific areas, however, which will be covered here; namely, 1) investigation of mixtures of mono sodium and mono potassium phosphate as the fluxing agent for high basis weight papers; 2) support of Japan Cigarette Development's efforts to develop a low sidestream product for the Japanese market; and 3) work directed toward a model with an intermediate sidestream reduction (about 40-50%)

For the 63 g/m^2 calcium carbonate papers, mono potassium phosphate has been an effective sizing agent with respect to sidestream reduction. However, the use of high levels of this sizing agent may cause problems in the commercial development of a paper, since the solubility of mono potassium phosphate in water is low enough to cause problems. Mono sodium phosphate is much more soluble. Consequently, if a mixture of the two salts were used, commercial paper production would be straightforward. Mixtures of mono sodium and mono potassium phosphate have been tested and can achieve the sidestream reduction and puff count targets. Subjective screening is being conducted for the mixed salts. If models with the mixed salts are subjectively acceptable, then we will respecify the composition of the paper.

Models have been made with four Kimberly-Clark high basis weight papers (E2557-E2560), two blends (Lark and L&M), and charcoal filters. Although the E2560 paper was preferred for these models, as was the case with Project Lotus models,

it has been decided to do further work with the E2559 paper (63 g/m^2 basis weight, 36% calcium carbonate, and 2.9 Coresta porosity) so that maximal sidestream reduction is achieved. Paper has been ordered with the appropriate level of mono potassium phosphate to make sufficient cigarettes for a Danchi test. In addition work will be continued to determine the explanation for the low visible sidestream levels for JTI cigarettes.

Cigarettes were made with 6-8% mono potassium phosphate on E2560 paper to achieve a 40-50% reduction in sidestream visibility in an attempt to realize better subjective performance at this intermediate level of visibility reduction. Subjective testing did not show significantly better performance at 45% reduction compared to models with 65% sidestream visibility reduction. Work with the high basis weight paper at intermediate visibility levels has been discontinued at this time.

b. Tactics and timetable

(1) Evaluate mixtures of mono sodium and mono potassium phosphate sizing agents with the preferred blend - second quarter, 1989.

(2) Provide appropriate papers for cigarettes for a second quarter Danchi test of a low sidestream prototype - first quarter, 1990.

(3) Evaluate hand-made single component cigarettes made from eight Japanese tobacco grades for sidestream production and static burn time - second quarter, 1989.

6. Characterize the chemistry of sidestream smoke from existing brands, new products and prototypes using the new sidestream chamber

a. Status

A system for determining total particle number and particle size distribution has been added to the sidestream chamber. A transmissometer, a device which can obtain visibility data, has also been added. The ammonia analysis is now a routine method, and the capability for aldehyde analysis (formaldehyde, acetaldehyde, and propionaldehyde) has been added. A nicotine study has been completed which has resulted in the construction of a decay curve. An equation to describe this decay curve is now being developed. Also, the study has shown that XAD collection of nicotine is superior to the use of Extralut. A study of the sidestream chemistry of high basis weight papers is now in progress.

Discussions are in progress to evaluate the potential use of the sidestream chamber to support Project Ambrosia. A decision should be reached by the end of February.

b. **Tactics and timetable**

(1) Complete study on models made from high basis weight papers - first quarter, 1990.

(2) Continue method development work using both the Chemical Research and Analytical Research chambers - continuing.

(3) Develop capability to monitor mainstream carbon monoxide, carbon dioxide, and TPM using the sidestream chamber while simultaneously measuring sidestream components - first quarter, 1990.

(4) Determine potential role of the sidestream chamber to support Project Ambrosia - March, 1990.

7. **Define the subjective and analytical characteristics of mainstream smoke from a calcium carbonate, dual wrap low sidestream prototype compared to an appropriate control**

a. **Status**

Although the primary objective of the low sidestream portion of the paper technology program is the development of a proprietary paper which will reduce visible sidestream smoke, it is of considerable importance to understand what changes in mainstream smoke have occurred in commercial low sidestream papers in order to appropriately design new low sidestream models for acceptable subjectives. Neither the Kimberly-Clark low sidestream calcium carbonate paper or the Ecusta magnesium hydroxide paper give acceptable subjectives on a full circumference cigarette. Models utilizing the KC paper tend to have a "dirty" off taste, whereas the Ecusta papers, and many other papers using magnesium compounds, are characterized by a harsh, metallic taste. Three sets of cigarettes have been made, each set containing a model with Marlboro blend and a model with 2I blend. The three sets are a control made with standard paper, an experimental model made with Ecusta 35% magnesium hydroxide paper, and an experimental model made with the double wrap system (KC 093 outer liner and PDM inner liner). Initial subjective screening confirmed that gross subjective differences among the models were present. The second phase of the work, detailed subjective analysis and basic analytical characterization of the mainstream smoke from each model, has also been completed except for a small number of analytical determinations. When the second phase has been completed, phase three, fractionation of gas phase or particulate into specific chemical classes, will be initiated. This work will

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start with a determination of a mainstream gas phase profile, separation of condensate into acid, base, and neutral fractions, and detailed gc/ms analysis of the acid and basic fractions.

b. Tactics and timetable

(1) Complete analytical evaluation of main stream smoke from both models and control - first quarter, 1990.

(2) Initiate detailed analytical study of mainstream smoke - second quarter, 1990.

III. Products for Aroma Modification of Sidestream

A. Objective

To develop a wrapper containing a vanillin-release agent.

B. Introduction and Status

In order to support Project Ambrosia regarding developing a paper containing a vanillin-release agent, it was necessary to prepare a proprietary material to avoid potential infringement with the Ecusta patent covering "flavor-release sugar glycosides." Such a compound was prepared through the base-catalyzed condensation of vanillin with ethyl phenylacetate (CR-2898). Subjective evaluation of cigarettes made from paper coated with this compound confirmed that the compound fulfilled the necessary requirements for a Chelsea "look alike." A three step synthesis of this material was developed, and the Aldrich Chemical Company was contacted in order to make sufficient material for test market. Work at Aldrich is in progress. During product development work with papers coated with this compound, it was noted that the material was photosensitive. The papers yellowed, particularly when subjected to light from a mercury vapor lamp. Although this complication was not expected, it was not surprising. Free phenols are known to undergo light catalyzed reactions, particularly under basic conditions. Apparently, the calcium carbonate filler in the cigarette paper is sufficiently basic. Further work has shown that with sufficient irradiation (two weeks in the slitter room under mercury vapor lamps) the compound is converted in about 80% yield to essentially a single yellow compound. Currently our challenge is two-fold - 1) to have sufficient amount of a vanillin-release agent in hand by the end of March for a potential test market, and 2) to redesign the compound to eliminate its photosensitivity. The following strategies have been developed to meet this challenge.

1. Prepare sufficient quantities of material at Aldrich to meet test market requirements.

2. Determine the extent of the "yellowing" problem.

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3. Develop an alternate vanillin-release agent which will not undergo photosensitized reaction.

C. **Tactics and Timetable**

1. **Prepare sufficient quantities of material at Aldrich to meet test market requirements.**

   a. A schedule has been worked at with Aldrich which calls for delivery of 6.5 pounds of CR-2898 in early March and an additional 25 pounds by March 22.

   b. Carry out detailed smoke chemistry studies to allow phase four clearance - March 15, 1990.

   c. Conduct paper coating trials with Ecusta to ensure that there will be no problems in coating test market quantities - March 15, 1990.

2. **Determine the extent of the "yellowing" problem.**

   a. Determine the extent of photochemical conversion as a function of time for various light sources including mercury vapor, metal halide, fluorescent, and sunlight - March 2, 1990.

   b. Identify the compound formed in the photochemical conversion - second quarter, 1990.

3. **Develop an alternate vanillin-release agent which will not undergo photosensitized reaction.**

   a. Block the vanillin hydroxyl group of CR-2898 with t-butyl carbonate and evaluate product subjectively - March 2, 1990.

   b. Optimize synthesis for blocked CR-2898 - April 1, 1990.

   c. Carry out detailed pyrolysis/gc/ms studies on blocked CR-2898 - April 15, 1990.

   d. Prepare sufficient blocked CR-2989 for run of machine-made cigarettes - May 1, 1990.

   e. Contract out synthesis of large quantities of blocked CR-2898 if required.

IV. **Project Tomorrow**

A. **Objective**

To develop special cigarette papers which will control the burn rate of a cigarette.

B. Introduction and Status

Work to date has shown that the burn rate of a cigarette can be retarded if some type of process is performed which results in bands of lower porosity on the cigarette paper. A paper of this type may have utility for Project Tomorrow. Two types of treatments are currently being investigated. The first involves treatment of normal cigarette paper with bands using either the gel phase of metal oxides or carbonates prepared by the sol-gel process or soluble phosphate burn retardants. Models made by hand-painting of sol-gel derived alumina gel gives a cigarette which burns more slowly in the treated area. A number of attempts have been made to coat paper with bands of two different sol-gels - the alumina sol-gel prepared at Lee Labs, and a magnesium hydroxide gel containing 3% alumina prepared at NY Poly. To date we have been unable to apply sufficient material using a rotogravure press to see any effect on mass burn rate. Similar problems have been encountered with both mono potassium and mono sodium phosphate. We are currently working to achieve an overall coating with the rotogravure press in order to compare mass burn rates of fully coated papers and banded papers at similar loading per unit area of paper. Problems have been encountered, however, in coating 25 g/m^2 basis weight papers caused by the low concentration of the solutions being used. It would appear at this time that the only viable material that can be used for this approach is mono sodium phosphate.

A second approach is to introduce bands of increased flax density where the additional flax contains no inorganic filler on the paper maker. Hand sheets have been made utilizing this approach, and results have been encouraging. However, at this time no method exists which would allow us to make paper with bands of this type commercially. A modified dandy roll has been designed which would allow the application of transverse bands of flax, or other fibers, on the Fourdrinier wire. Detailed drawings of parts is now in progress. When all necessary parts have been obtained, the apparatus will be installed on the pilot paper maker at the University of Maine.

The two strategies currently being pursued for Project Tomorrow are:

1. Prepare bobbins of paper for Project Tomorrow with transverse bands of mono sodium phosphate on the paper.

2. Develop potential methodology for applying dense flax bands to cigarette paper at the paper-making machine.

C. Tactics and Timetable

1. Prepare bobbins of paper for Project Tomorrow with transverse bands of mono sodium phosphate on the paper.

a. Overall coat standard cigarette paper with a highly concentrated solution of mono sodium phosphate at two levels achieved by one and two passes on a rotogravure press - second quarter, 1990.

b. Apply transverse bands of mono sodium phosphate at the same levels as in (a) using a rotogravure press - second quarter, 1990.

c. Compare burn rate of cigarettes made from papers produced in (a) and (b) - second quarter, 1990.

2. **Develop potential methodology for applying dense flax bands to cigarette paper at the paper-making machine.**

a. Complete detailed drawings, and ordering and machining of parts for modified dandy roll - March 7, 1990.

b. Build modified dandy roll on to University of Maine pilot paper making machine - March 21, 1990.

c. Carry out trials at University of Maine for the production of bobbins of paper containing transverse flax bands - second quarter, 1990.

V. PM Web

A. Objective

To support the Filter Research and Development Program through the development of a CA web type material by the third quarter of 1990.

B. Introduction and Status

Paper filters have been shown to have a greater filter efficiency as compared to CA tow at equal filter RTDs. However, paper filters suffer from a subjective disadvantage compared to CA. Some time ago Celanese sampled us with a filter material they call CA web. This material is manufactured through a paper making process. A proprietary material Celanese calls fibrets enables a sheet to be made on a Fourdrinier wire. CA web is an extremely interesting material in that it appears to have the same filtration properties as paper, but the subjective response of CA. Unfortunately it appears that it will be at least two years, if not longer, before CA web can be commercialized. As a consequence the Paper Technology group has been asked to assist the Filter Research and Development group in the development of an alternative to CA web.

Three approaches are currently being investigated. The first involves the formation of PM web. This material is made from 75% cut (1/4") CA staple and 25% softwood fiber. The softwood fiber provides sufficient hydrogen bonding to allow a paper web to be formed on a Fourdrinier wire. Considerable work has been done in the hand sheet lab with this material, and several bobbins, varying only in the extent

of softwood fiber refining, have recently been made at the University of Maine.

The second approach will investigate coating of paper filter web with both cellulose acetate and triacetin. Arrangements have been made at the James River Paper Company to coat the filter paper with acetone solutions of both materials. In order to move as rapidly as possible on this approach, we will use the most appropriate rotogravure cylinder James River has available which will provide only 80% coverage. If results are promising, we will have a ten inch cylinder made, and repeat the work on a larger scale.

The third approach is still in the research stage and would appear difficult to commercialize to date. This approach involves acetylation of the paper surface. Promising results have been obtained using acetic anhydride and potassium carbonate as the acetylation medium in the laboratory. However, the time required to achieve the desired degree of surface acetylation, two hours, is far too long to allow for a commercial process to be developed. An initial trial with a much more active catalyst, sulfoacetic acid, led to disintegration of the paper. Although work on this approach will continue for the present, it will be terminated if results from the coating trials are sufficiently encouraging.

As can be seen, the three strategies being employed to achieve the stated objective are:

1. Utilize paper making technology to form a filter material consisting of an appropriate mixture of CA and cellulose fiber.

2. Coat filter paper web with CA and/or triacetin to form a filter material with filtration properties similar to paper and subjective properties similar to CA.

3. Develop a technique for surface acetylation of filter paper web which can be commercialized.

C. **Tactics and Timetable**

1. **Utilize paper making technology to form a filter material consisting of an appropriate mixture of CA and cellulose fiber.**

   a. Evaluate filters made from PM web at the University of Maine - second quarter, 1990.

   b. Utilize information gained from (a) above to optimize PM web at the University of Maine - second quarter, 1990.

2. **Coat filter paper web with CA and/or triacetin to form a filter material with filtration properties similar to paper and subjective properties similar to CA.**

   a. Coat filter paper web with acetone solutions of CA and triacetin at James River - February 19, 1990.

b. Evaluate filters made from coated papers - second quarter, 1990.

c. If results from (b) above are promising, fabricate ten inch rotogravure cylinder and coat papers with a range of concentrations of CA and/or triacetin - second quarter, 1990.

3. **Develop a technique for surface acetylation of filter paper web which can be commercialized.**

a. Continue experiments with sulfoacetic acid - second quarter, 1990.

b. Investigate other catalysts and solvents for acetylation reaction - second quarter, 1990.

c. Contact recommended paper manufacturers to discuss potential commercialization of such a process - second quarter, 1990.

Appendix A

It is anticipated at this time that the majority of the effort for the Paper Technology Program after 1990 will be in the area of reduced sidestream and Project Tomorrow. However, it is also anticipated that much of the effort devoted to the reduced sidestream program will shift to the second objective; namely, the development of papers which can reduce sidestream odor and irritation. During the next six months a plan will be developed to address this issue. This plan will involve the following strategies:

1. Identify chemical classes of compounds which are responsible for sidestream odor and irritation.

2. Investigate the effect of known catalysts incorporated into the wrapper on sidestream odor and irritation.

3. Investigate the effect of substances which are known to react with aldehydes, amines, and sulfur compounds on sidestream odor and irritation when incorporated into the wrapper.

4. Establish an objective method for determining sidestream irritation.

5. Rank blend components using single component cigarettes with regard to sidestream odor and irritation.

6. Collaborate closely with personnel in Project Ambrosia regarding the effects of specific flavorants on sidestream odor.